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(11) **EP 0 960 958 A2**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
01.12.1999 Bulletin 1999/48

(51) Int. Cl.<sup>6</sup>: **C23C 16/30**, H01L 21/00

(21) Application number: 99110260.9

(22) Date of filing: 27.05.1999

(84) Designated Contracting States:  
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE  
Designated Extension States:  
AL LT LV MK RO SI

(30) Priority: 29.05.1998 US 86811

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(54) **Method for producing hydrogenated silicon oxycarbide films**

(57) This invention is a method for producing hydrogenated silicon oxycarbide (H:SiOC) films having a low dielectric constant. This method comprises reacting an methyl-containing silane in a controlled oxygen environment using plasma enhanced or ozone assisted chemical vapor deposition to produce said films. The resulting films are useful in the manufacture of semiconductor devices and have a dielectric constant of 3.6 or less.

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## Description

[0001] The use of chemical vapor deposition (CVD) to produce  $\text{SiO}_2$ , SiNC or SiC thin films on semiconductor devices from silicon-containing materials is well known in the art. Chemical vapor deposition processes typically comprise introducing the gaseous silicon-containing material and a reactive gas into a reaction chamber containing the semiconductor substrate. An energy source such as thermal or plasma induces the reaction between the silicon-containing material and reactive gas thereby resulting in the deposition of the thin film of  $\text{SiO}_2$ , SiNC or SiC on the semiconductor device. Plasma enhanced chemical vapor deposition (PECVD) is typically carried out at low temperatures ( $<500^\circ\text{C}$ .) thereby making PECVD a suitable means for producing dielectric and passivation films on semiconductor devices. Silicon-containing materials include silane ( $\text{SiH}_4$ ), tetraethyl orthosilicate (TEOS), silacyclobutanes and alkylsilanes such as trimethylsilane.

[0002] The use of methyl-containing silanes to produce silicon dioxide ( $\text{SiO}_2$ ), amorphous SiNC and silicon carbide (SiC) films by chemical vapor deposition is known in the art. For example, U.S. Patent 5,465,680 discloses a method for making crystalline SiC films. The method comprises heating the substrate  $600^\circ\text{C}$ . to  $1000^\circ\text{C}$ ., and thereafter exposing the substrate to trimethylsilane in a standard chemical vapor deposition process. EP Application 0 774 533 discloses a method of making  $\text{SiO}_2$  coatings from the CVD of a reactive gas mixture comprising an organosilicon material and an oxygen source. EP Application 0 771 886 discloses a method of making SiNC coating from the CVD of a reactive gas mixture comprising an organosilicon material and a nitrogen source.

[0003] As semiconductor device structures become increasingly smaller the dielectric constant as well as the integrity of the film become important. Films produced by known CVD processes have high dielectric constants (i.e. 3.8 or greater). Therefore there is a need for processes and materials that result in low dielectric constant films. A new deposition processes known as Low-k Flowfill<sup>®</sup>, produces films having a dielectric constant of  $<3.0$ . This method uses a chemical vapor deposition reaction between methylsilane and hydrogen peroxide to produce a methyl doped silicon oxide film (See S. McClatchie, K. Beekmann, A. Kiermasz; Low Dielectric Constant Oxide Films Deposited Using CVD Techniques, 1988 DUMIC Conference Proceedings, 2/98, p. 311-318). However, this process requires a non standard CVD system, the use of a lower stability oxygen source (hydrogen peroxide) and generates water as a by-product which can be undesirable in semiconductor devices.

[0004] An object of this invention is to provide a method for producing low dielectric constant thin films of hydrogenated silicon oxycarbide by chemical vapor deposition.

[0005] This invention pertains to a method of producing thin films of hydrogenated silicon oxycarbide ( $\text{H:SiOC}$ ) having low dielectric constants on substrates, preferably semiconductor devices. The method comprises the plasma enhanced or ozone enhanced chemical vapor deposition of a reaction mixture comprising a methyl-containing silane and an oxygen providing gas. By controlling the amount of oxygen available during the reaction/deposition process a film comprising hydrogen, silicon, carbon and oxygen is produced. These films typically have a dielectric constant of 3.6 or less and are particularly suited as interlayer dielectrics.

[0006] This invention pertains to a method for producing hydrogenated silicon oxycarbide films on substrate, preferably semiconductor substrates. The method for producing the films comprises the chemical vapor deposition reaction of a reactive gas mixture comprising an alkylsilane and an oxygen providing gas wherein the amount of oxygen present during the reaction is controlled. By "semiconductor substrate", it is meant to include silicon based devices and gallium arsenide based devices intended for use in the manufacture of a semiconductor components including focal plane arrays, opto-electronic devices, photovoltaic cells, optical devices, transistor-like devices, 3-D devices, silicon-on-insulator devices and super lattice devices. Semiconductor substrates include integrated circuits preferably in the wafer stage having one or more layers of wiring or integrated circuits before the application of any metal wiring.

[0007] The hydrogenated silicon oxycarbide films produced herein are represented by the general formula  $\text{Si}_w\text{O}_x\text{C}_y\text{H}_z$  where w has a value of 10 to 33, preferably 18 to 20 atomic %, x has a value of 1 to 66, preferably 18 to 21 atomic %, y has a value of 1 to 66, preferably 31 to 38 atomic % and z has a value of 0.1 to 60, preferably 25 to 32 atomic %; and  $w + x + y + z = 100$  atomic %.

[0008] The hydrogenated silicon oxycarbide films are produced from a reactive gas mixture comprising a methyl-containing silane and an oxygen providing gas. Methyl-containing silanes useful herein include methylsilane ( $\text{CH}_3\text{SiH}_3$ ), dimethylsilane ( $(\text{CH}_3)_2\text{SiH}_2$ ), trimethylsilane ( $(\text{CH}_3)_3\text{SiH}$ ) and tetramethylsilane ( $(\text{CH}_3)_4\text{Si}$ ), preferably trimethylsilane.

[0009] A controlled amount of oxygen is present in the deposition chamber. The oxygen may be controlled by the type of oxygen providing gas used, or by the amount of oxygen providing gas that is used. If too much oxygen is present in the deposition chamber a silicon oxide film with a stoichiometry close to  $\text{SiO}_2$  will be produced and the dielectric constant will be higher than desired. Examples of oxygen providing gases are air, ozone, oxygen, nitrous oxide, nitric oxide, carbon monoxide and carbon dioxide, preferably nitrous oxide. The amount of oxygen providing gas is typically less than 5 volume parts oxygen providing gas per volume part of methyl-containing silane, more preferably from 0.1 to 4.5 volume parts of oxygen providing gas per volume part of methyl-containing silane. One skilled in the art will be able to readily determine the amount of oxygen providing gas based on the type of oxygen providing gas and the deposition

conditions.

[0010] Other materials may be present in the reactive gas mixture. For example, carrier gases such as helium or argon, dopants such as phosphine or diborane, halogens such as fluorine or any other material that provides additional desirable properties to the film may be present.

[0011] The reactive gas mixture is introduced into a deposition chamber containing a substrate, preferably a semiconductor substrate, wherein the reaction between the methyl-containing silane and oxygen providing gas is induced resulting in the deposition of a film on the substrate wherein the film comprises hydrogen, silicon, carbon and oxygen and has a dielectric constant of 3.6 or less on the substrate. Any chemical vapor deposition (CVD) method which has a substrate temperature of less than 500°C. may be used. Temperatures greater than 500°C. are typically not suitable for semiconductor substrates, in particular semiconductor substrates having aluminum wiring. Plasma enhanced chemical vapor deposition (PECVD) is preferred due to the low temperatures that can be used and its wide use in the industry. Ozone enhanced CVD may also be used.

[0012] In PECVD, the gas mixture is reacted by passing it through a plasma field. The plasmas used in such processes comprise energy derived from a variety of sources such as electric discharges, electromagnetic fields in the radio-frequency or microwave range, lasers or particle beams. Generally preferred in the plasma deposition processes is the use of radio frequency (10 kHz to 10<sup>2</sup> MHz) or microwave (1.0 to 10 GHz) energy at moderate power densities (0.1 to 5 watts/cm<sup>2</sup>). The specific frequency, power and pressure, however are generally tailored to the equipment. Preferably the films are produced using PECVD at a power of 20 to 1000 W; a pressure of 1 to 10,000 mTorr (0.0133 to 1132.2 Pa); and a temperature of 25 to 500°C. Confined, low pressure (1-5 mTorr) microwave frequency plasmas, often referred to as high density plasmas, can be combined with a RF frequency excitation in a process which helps planarize a varying surface topography during CVD growth. This process is useful in the formation of interlayer dielectrics.

[0013] The films produced herein may be of varying thicknesses. Films having thicknesses of 0.01 to 10 µm may be produced by the method of this invention. Preferably, the films have a thickness of 0.5 to 3.0 µm.

[0014] One advantage to the instant method is that when nitrous oxide is used as the oxygen providing gas, the film composition and properties remain essentially the same even when the amount of nitrous oxide in the reactive gas mixture is significantly varied (1.2:1 to 4.5:1 volume parts N<sub>2</sub>O to methyl-containing silane).

[0015] Another advantage to the method of this invention is the ability to link successive growth processes to produce multilayer structures for example of SiO<sub>2</sub>/H:SiOC/SiO<sub>2</sub> or SiC:H/H:SiOC/SiC:H by increasing or deleting the oxygen providing gas at the appropriate time during the CVD process. It is preferred to produce discreet layers by stopping the reactive gas flow, adjusting the amount of oxygen providing gas and thereafter resuming the reactive gas flow to produce the next layer.

[0016] The films produced, due to the low dielectric constant, are particularly suited as interlayer dielectrics in semiconductor integrated circuit manufacturing such as gate dielectrics, premetal and intermetal dielectrics and passivation coatings. The films produced have a dielectric constant of 3.6 or less, preferably, 3.2 or less, more preferably 3.0 or less.

### Examples

[0017] So that those skilled in the art can understand and appreciate the invention taught herein, the following examples are presented.

[0018] In Examples 1-9 and Comparative Examples 1-2, dielectric properties were measured using metal-insulator-semiconductors (Examples 4-9) and metal-insulator-metal capacitors (Examples 1-3, Comparative Examples 1-2). Measurements were performed immediately after the metal gate deposition (top electrode) and again after one or more anneal cycles in N<sub>2</sub> in the temperature range of 350 to 400°C. Relative permittivity, K, was calculated from the capacitor geometry and the film thickness. Flow rates are shown in the tables as sccm (standard cm<sup>3</sup>/min.)

### EXAMPLES 1-9

[0019] A reactive gas mixture comprising trimethylsilane (3MS) and nitrous oxide (See Tables 1 and 2 for gas flow amounts) was introduced into a capacitively coupled parallel plate PECVD system using thermally oxidized (0.1 µm SiO<sub>2</sub>) silicon wafers coated with 0.5 µm Al or bare silicon wafers as the substrates. The PECVD system was operated at a power of 350 W, pressure of 2700 mTorr (359.69 Pa) and temperature of 250°C, Helium was used as a carrier gas. The dielectric constant, growth rate and film stress (compressive) results for Examples 1-9 are in Tables 1 and 2. The composition and density of the films produced in Examples 4-9 are in Table 3. As can be seen in Table 2, even when the amount of nitrous oxide is significantly varied, the resulting films have essentially the same composition and properties.

Table 1

Example No.	3MS (sccm)	He (sccm)	N <sub>2</sub> O (sccm)	K (MIM)	K (400°C. post metal anneal)	Growth Rate (Å/min)	Stress* (MPa)
1	100	380	120	3.6	3.6	535	61 C
2	100	260	240	3.4	3.1 to 3.4	1531	28 C
3	100	140	360	3.2	2.8-3.0	3615	53 C

\*C = compressive stress

Table 2

Example No.	3MS (sccm)	He (sccm)	N <sub>2</sub> O (sccm)	K (MIS)	K (post metal anneal*)	Growth Rate (Å/min)
4	100	380	120	3.2	3.1	624
5	100	260	240	3.1	3.0	2076
6	100	140	360	3.1	3.1	4830
7	100	100	400	3.0	2.9	5510
8	100	50	450	3.1	3.0	6076

\* three cycles, one hour soak each, 200-350-200°C., 200-400-200°C., 200-400-200°C.

Table 3

Example No.	Thickness (μm)	Si atom%	H atom%	C atom%	O atom%	Density g/cm <sup>3</sup>
4	0.62	0.20	0.25	0.37	0.18	1.46
5	0.83	0.18	0.29	0.35	0.18	1.34
6	0.97	0.2	0.3	0.31	0.19	1.36
7	1.10	0.18	0.29	0.33	0.20	1.36
8	1.22	0.18	0.27	0.34	0.21	1.36

**COMPARATIVE EXAMPLES 1-2**

[0020] Using the same procedure for Examples 1-8, a reactive gas mixture comprising trimethylsilane and oxygen were used in the plasma enhanced chemical vapor deposition. Results are given in Table 4. The resulting films were essentially SiO<sub>2</sub> films because of the high amount of oxygen used in the reactive gas mixture.

Table 4

Example No.	3MS (sccm)	He (sccm)	O <sub>2</sub> (sccm)	K (MIM)	K (400°C. post metal anneal)	Growth Rate (Å/mm)	Stress* (MPa)
C1	100	440	60	4.6	-	1456	60 T
C2	100	380	120	5.8	-	2481	71 T

\* T = tensile stress

**COMPARATIVE EXAMPLE 3**

**[0021]** This example is Example 3 of EP Application 0 774 533. A reactive gas mixture comprising 6 sccm of trimethylsilane (TMS) and 523 sccm of nitrous oxide was introduced into a capacitively coupled parallel plate PECVD system using silicon wafers as the substrates. The PECVD system was operated at a power of 50 W, a pressure of 1000 mTorr and a temperature of 300°C. Helium (500 sccm) was used as a carrier gas. Due to the high amount of nitrous oxide (N<sub>2</sub>O) being used, the resulting film was a SiO<sub>2</sub> film.

**Claims**

1. A method for producing hydrogenated silicon oxycarbide films comprising

introducing a reactive gas mixture comprising a methyl-containing silane and an oxygen providing gas into a chemical vapor deposition chamber containing a substrate and inducing a reaction between the methyl-containing silane and the oxygen providing gas at a temperature of 25°C. to 500°C.;  
wherein there is a controlled amount of oxygen present during the reaction to provide a film comprising hydrogen, silicon, carbon and oxygen having a dielectric constant of 3.6 or less on the substrate.

2. The method of claim 1 wherein the methyl-containing silane is selected from methylsilane, dimethylsilane, trimethylsilane and tetramethylsilane.

3. The method of claim 1 wherein the oxygen providing gas is selected from air, ozone, oxygen, nitrous oxide, nitric oxide, carbon monoxide and carbon dioxide.

4. The method of claim 1 wherein the methyl-containing silane is trimethylsilane and the oxygen providing gas is nitrous oxide.

5. The method of any of claims 1-4 wherein the amount of oxygen providing gas is less than 5 volume parts oxygen providing gas per one volume part of methyl-containing silane.

6. The method of any of claims 1-5 wherein reaction is induced by exposing the reactive gas mixture to plasma.

7. The method of any of claims 1-6 wherein the reactive gas mixture additionally comprises a carrier gas.

8. The method of any of claims 1-7 wherein the hydrogenated silicon oxycarbide film has a thickness of 0.01 to 10 μm.

9. The method of claims 1-8 wherein the substrate is a semiconductor substrate.

10. The method of claims 1-7 wherein the amount of oxygen providing gas is increased or decreased during the reaction between the methyl-containing silane and the oxygen providing gas to produce a film containing successive layers selected from the group consisting of SiO<sub>2</sub>, H:SiOC and SiC:H.

11. The method of claim 6 wherein the reaction is induced by exposing the reactive gas mixture to plasma at a power of 20 to 1000 W, a pressure of 1 to 10,000 mTorr (0.0133 to 1332.2 Pa), and a temperature of 25 to 500°C.

12. The method of claim 6 wherein the reaction is induced by exposing the reactive gas mixture to confined, low pres-

sure microwave frequency plasma combined with radio frequency excitation.

13. The method of any of the preceding claims wherein the hydrogenated silicon oxycarbide film has the formula  $\text{Si}_w\text{O}_x\text{C}_y\text{H}_z$ , where w has a value of 18 to 20 atomic %, x has a value of 18 to 21 atomic %, y has a value of 31 to 38 atomic % and z has a value of 25 to 32 atomic %; and  $w + x + y + z = 100$  atomic % .

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